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14. ABSTRACT

There has been significant interest in recent years in the combustion of sub-micron aluminum particles, and the standard theoretical framework is the shrinking-core model. This model, in the context of any fuel, has roots that go back 60 years, [1]. A common reference is a chapter in [2], although the discussion there, within a framework of global statements, is reminiscent of well stirred reactor discussions, familiar in the chemical engineering literature, so that certain details are obscured. However, the model is simply described: A spherical core of liquid aluminum is surrounded by a shell of alumina and the aluminum core shrinks as aluminum is converted to alumina at the metal/oxide interface. The conversion occurs because of the inward transport of O atoms (we assume that the surrounding atmosphere is air) from the outer boundary of the oxide shell. It is commonly assumed that this transport is solely diffusive in nature, and quasi-steady, at best an approximation; and that apart from the aluminum/oxide transformation, the geometry is fixed. Provided these approximations only lead to modest error it might be reasonably argued ! that it is acceptable in view of two significant uncertainties: the value of the diffusion coefficient of the O atoms; and the value of the O concentration within the oxide at the oxide boundary. However, as we shall see, one of the neglected ingredients has significant mechanical consequences in the context of the spherical geometry, and therefore it is important to consider it. Because of the mechanical consequences, an analytical treatment in the spherical geometry is not possible, and yet analytical treatments are of great value in revealing fundamental physics. ! And so we shall start our discussion with a planar model, purely because of the insights thereby achieved, not because it corresponds to a configuration to be found in the physical world.

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An Examination of the Shrinking-Core Model of Sub-Micron Aluminum Combustion

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September 14, 2012

1 Introduction

There has been significant interest in recent years in the combustion of sub-micron aluminum particles, and the standard theoretical framework is the shrinking-core model. This model, in the context of any fuel, has roots that go back 60 years, [1]. A common reference is a chapter in [2], although the discussion there, within a framework of global statements, is reminiscent of well-stirred reactor discussions, familiar in the chemical engineering literature, so that certain details are obscured. However, the model is simply described: A spherical core of liquid aluminum is surrounded by a shell of alumina and the aluminum core shrinks as aluminum is converted to alumina at the metal/oxide interface. The conversion occurs because of the inward transport of O atoms (we assume that the surrounding atmosphere is air) from the outer boundary of the oxide shell. It is commonly assumed that this transport is solely diffusive in nature, and quasi-steady, at best an approximation; and that apart from the aluminum/oxide transformation, the geometry is fixed. Provided these approximations only lead to modest error it might be reasonably argued that it is acceptable in view of two significant uncertainties: the value of the diffusion coefficient of the O atoms; and the value of the O concentration within the oxide at the oxide boundary. However, as we shall see, one of the neglected ingredients has significant mechanical consequences in the context of the spherical geometry, and therefore it is important to consider it.
Because of the mechanical consequences, an analytical treatment in the spherical geometry is not possible, and yet analytical treatments are of great value in revealing fundamental physics. And so we shall start our discussion with a planar model, purely because of the insights thereby achieved, not because it corresponds to a configuration to be found in the physical world.

2 The Planar Problem

The configuration is sketched in Figure 1. Liquid aluminum occupies the interval $0 < x < x_{al.}$, alumina occupies the region $x_{al.} < x < x_{oxd.}$. The interface between the two materials, also the

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reaction front, moves to the left with speed v_{rf}. the oxide moves as a solid body to the right with speed v. The $\dot{M}$ are mass fluxes (of O atoms, aluminum, oxide) to or from the front, measured relative to the front.

This model does not account for aluminum diffusion, only diffusion of the O atoms. If diffusion of both occurs the reaction would occur interior to the alumina either at a front or within a spread-out reaction zone. There are various references to (and opinions about) aluminum diffusion in the literature.

Campbell et al, [3] carry out molecular dynamics simulation in which they consider a ball of aluminum atoms of diameter 20nm exposed to an oxygen atmosphere and observe oxide layer growth with diffusion of both aluminum and oxygen. They claim that the alumimum diffusion is greater than that of the oxygen because of the smaller steric size of the aluminum atoms. But the temperature is 300K so that the aluminum is solid, and here we are concerned with liquid aluminum; in the rocket business the interest is in aluminum particles released into the hot rocket chamber.

Rai et al, [4] claim that when the aluminum is solid, oxygen diffusion alone occurs; when the alumimum is liquid both aluminum and oxygen diffusion occur. For evidence they note that they get hollow post-burn oxide particles when the temperatures are high enough for the aluminum to be in the molten state. This is an interesting argument, but if one carries out a standard shrinking-core model analysis, with an interior reacting front, and invokes Ockham's Razor - the volume of the aluminum sphere changes precisely to accommodate the outward aluminum diffusion - this leads naturally to a solution sans interior void. To get a void one would need to move the outer boundary of the aluminum inward more slowly but how one would specify that modification is unknown. Note that an appeal to the steric argument to justify that alumimim diffusion will occur ignores other physical ingredients. The atoms at a liquid surface are tied by atomic forces, and an atom will only detach from the surface when the sum of the collision forces from its neighbors is sufficient; sufficiency is a function of the temperature. And should a central void be inclined to arise the pressure there will be small, provided by aluminum vapor, and there will be a positive radial pressure gradient in the liquid which will also discourage surface detachment of atoms.

Trunov et al, [5] divide the oxidation process into two stages. At early times the oxide is amorphous in nature and is generated by aluminum diffusion. But the amorphous layer is only stable for thickness up to 5nm, and after that the γ crystalline form is generated (crystal size 5nm), generated by O diffusion. The α crystal state might occur later (crystal size 45nm) but only for large drops. However, these conclusions are rooted in experiments for slow oxidation, not the fast oxidation that is of interest to us.

Our conclusion is that the role of aluminum diffusion for our problem is, as yet, unknown, and our choice at this time is to ignore it. In a later study we shall revisit this question, partly because of the possibility that aluminum diffusion plays a role in transition solutions leading to the classical drop burning regime.

Returning to Figure 1, the two speeds are measured in the laboratory frame tied to $x = 0$. The speed v arises from mass conservation at the reaction front where, overall,

$$\begin{array}{ccccc} 2Al & + & 3O & \rightarrow & Al_2O_3 \\ (54) & & (48) & & (102) \end{array} \tag{1}$$

(We shall henceforth use α=54, β=48, and γ=102 so that our results can be understood in other

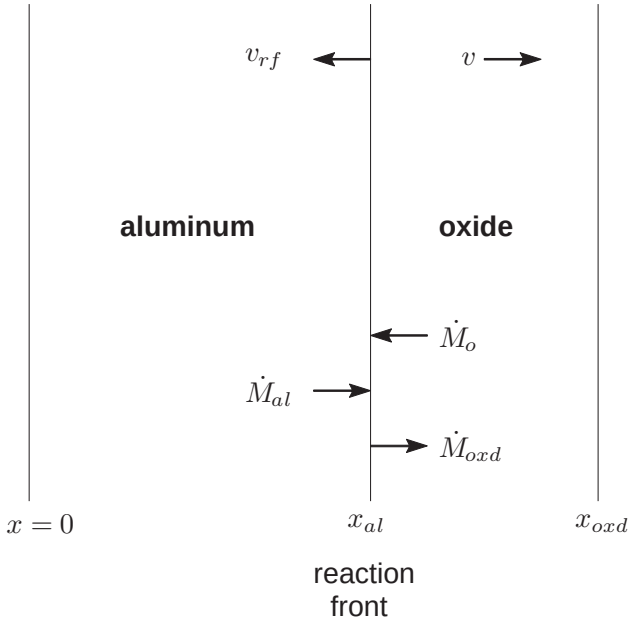

Figure 1: Configuration. v and v_{rf} are measured in the laboratory frame; all $\dot{M}$ are measured relative to the reaction front.

contexts.) Then if in a frame attached to the front the mass flux of O to the front is $\dot{M}_o$, the mass flux of aluminum to the front is $\dot{M}_{al.}$, and the mass flux of oxide away from the front is $\dot{M}_{oxd.}$ (then all the $\dot{M}$ are positive) we have

$$\frac{\dot{M}_{al.}}{\dot{M}_o} = \frac{\alpha}{\beta} \quad \text{and} \quad \frac{\dot{M}_{oxd.}}{\dot{M}_{al.}} = \frac{\gamma}{\alpha} \tag{2}$$

Now

$$\dot{M}_{al.} = \rho_{al.} v_{rf} \tag{3}$$

and

$$\dot{M}_{oxd.} = (v + v_{rf})\rho_{oxd.} \tag{4}$$

Also, accounting for both convection and diffusion of O,

$$\dot{M}_o = -(v + v_{rf})c + \mathsf{D}\frac{\partial c}{\partial x} \tag{5}$$

where c is the concentration of O atoms (in dimensions that of density). Here we shall assume that the reaction is fast, and is controlled by diffusion, so that at the front $c = 0$. Then

$$\dot{M}_o|_{\text{fast chem.}} = \mathsf{D}\frac{\partial c}{\partial x} \tag{6}$$

Within the oxide, c satifies the equation

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} = \mathsf{D}\frac{\partial^2 c}{\partial x^2} \tag{7}$$

Note that we neglect convective fluxes of c relative to the oxide which could only arise because of pressure gradients. Reference 4 accounts for pressure gradients, motivated by the simulations of Reference 3, and we shall say something about general stresses in a later section when we consider the spherical geometry.

Insofar as the oxide speed v is concerned, we have yet to come across any explicit discussion of it, although its physical origins and one of the important roles that it plays have long been recognized by corrosion scientists. If a thin layer of metal is converted to an oxide layer of greater volume, as in the case of aluminum, this converted layer will push out previously generated layers. And in the case of curved displaced layers, hoop stresses will be generated. Corrosion scientists are only interested in thin surface layers, [6, 7, 8]. More recently this phenomenon has been recognized by those concerned with aluminum drop ignition, [9], and here also it is only thin layers of surface oxide that are of interest. Our interests go deeper than that, literally.

It should be noted that Ref [9] proposes a model of sub-micron aluminum combustion that is quite different from the shrinking-core model. It is rooted in the idea that genesis layers of oxide violently rupture when heated rapidly, leading to an expansion wave which propagates into the core so that liquid aluminum is violently expelled in atomic sized clusters of naked aluminum which is rapidly consumed. The fundamental argument is a thermal one, quite independent of combustion, and Lynch et al, [10], subjected particles to the high temperature behind a reflected shock in an

inert (argon) atmosphere and spectrally examined the post shock gases. They found no trace of aluminum vapor for temperatures below 2300K.

Returning to equation (7), for the moment we shall adopt the quasi-steady approximation, neglecting the time derivative. Provided dynamical ingredients are not at the heart of a physical problem this can often be a useful approximation, providing valuable insights, albeit with quantitative error. We shall retain the time derivatives in numerical calculations reported later in the paper.

The general solution is

$$c = A + B \exp\left[\frac{v}{\mathsf{D}} x\right] \tag{8}$$

for arbitrary constants A and B to be determined from the boundary conditions

$$c = 0 \quad \text{at} \quad x = x_{al.} \qquad \text{and} \qquad c = c_o \quad \text{at} \quad x = x_{oxd.} \tag{9}$$

As noted earlier, the determination of c_o is difficult. O atoms are generated by collision of oxygen molecules with the aluminum surface, collide themselves with the surface, and a certain fraction attach and subsequently pass into the alumina between the alumina molecules. The gas phase processes are not in the continuum domain for there is a Knudsen layer at the drop/particle surface.

With c then specified as a function of $v, \mathsf{D}, c_o, x_{al.}$ and $x_{oxd.}$ equations (6), (3) and (2) yield

$$\dot{M}_o = v c_o \left[\exp \frac{v}{\mathsf{D}}(x_{oxd.} - x_{al.}) - 1\right]^{-1} = \frac{\beta}{\alpha}\dot{M}_{al.} = \frac{\beta}{\alpha}\rho_{al.} v_{rf} \tag{10}$$

Now

$$\frac{dx_{al.}}{dt} = -v_{rf} \qquad \text{and} \qquad \frac{dx_{oxd.}}{dt} = v \tag{11}$$

where, from (4), (3), and (2)

$$v = \left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}} - 1\right] v_r f \tag{12}$$

With $\rho_{al.}$=2400 kg/m^3, $\rho_{oxd.}$=3950 kg/m^3 the constant coefficient on the rhs is 0.148 for the aluminum problem.

Equations (12), (11), and (10) define equations for $x_{al.}$ and $x_{oxd.}$ from which we can deduce

$$x_{oxd.} - x_{oxd.}|_0 = -[x_{al.} - x_{al.}|_0] \left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}} - 1\right] \tag{13}$$

where

$$x_{oxd.}|_0 = x_{al.}|_0 = L \tag{14}$$

the initial thickness of the aluminum. And

$$(x_{al.} - L)^2 = 2\Lambda t \tag{15}$$

where

$$\Lambda = \mathsf{D}\Gamma^{-1}[1+\Gamma]^{-1}\ln\left[1+\frac{\alpha}{\beta}\frac{c_o}{\rho_{al.}}\Gamma\right]$$
$$\Gamma = \frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}} - 1 \tag{16}$$

Since c_o is three orders of magnitude smaller than $\rho_{al.}$, the logarithm function can be replaced by a linear approximation, whence

$$\Lambda \approx \mathsf{D}(1+\Gamma)^{-1}\frac{\alpha}{\beta}\frac{c_o}{\rho_{al.}} \tag{17}$$

At the end of the burn, when $x_{al.}$=0, $t = t_{\rm burn} \propto L^2$ a "$d^2 - t$" law in the vocabulary of fuel-drop burning. The formula is

$$t_{\rm burn} = \frac{L^2}{2}\frac{\beta}{\alpha}\frac{\rho_{al.}}{c_o}\frac{(1+\Gamma)}{\mathsf{D}} \quad \text{(fast chemistry, quasi-steady)} \tag{18}$$

A $d^2 - t$ law arises for a simple dimensional reason for the only way to define a time is L^2/D (cf. (15), (16). As noted earlier, the specification of D is challenging, but if the burn-law is essentially a $d^2 - t$ law an order-of-magnitude estimate for D is $L^2/t_{\rm burn}$. an estimate that will be valid for the spherical geometry with L equal to the particle/drop diameter.

For the same dimensional reasons the $d^2 - t$ law arises in the classical model of external flame fuel-drop burning in which the flame is essentially described by the Burke-Schumann limit. Sufficiently large aluminum drops will essentially burn in this fashion, modified slightly by the presence of an alumina cap on the aluminum ball. A thorough review of super-micron sized drop burning is presented in [11], and Figure 1 of that paper shows burning times vs diameter from 12 experimental studies, with diameters ranging from about 16 microns to 800 microns. There is substantial scatter in the combined data, but a best fit corresponds to a $d^{1.99} - t$ law. We know that when the flame temperature is greater than the ambient, the theoretical burning response of maximum temperature vs Damkohler number (proportional to d^2) is S-shaped with most observed burning occurring on the upper branch. Then a reduction of the Damkohler number will lead to quenching when the upper branch ends unless the ambient temperature is large enough to sustain significant evaporation of the aluminum so that combustion can continue on the lower branch. Thus at an ambient temperature of 1500K, for example, sufficiently small drops can not burn classically; on the other hand submicron drops can burn at that temperature in an internal combustion context. The nature of the transition zone, whether or not one always exists even, is not understood at the present time. Lynch et al, [12], examined 3-11 micron drops at temperature greater than 2400K, and therefore greater than the melting temperature of alumina. They used a variety of atmospheres and obtained $d^n - t$ laws for n between 1.3 and 0.2.

Returning to the solution summarized by equations (15) and (16) we can write down formulas for the speeds. We have

$$v_{rf} = \sqrt{\frac{\Lambda}{2t}} \tag{19}$$

and

$$v = \left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}} - 1\right]\sqrt{\frac{\Lambda}{2t}} \tag{20}$$

The singularity at $t = 0$ arises because at $t = 0$ we have $c = c_o$ at $x = x_{oxd.}|_0$ and $c = 0$ at $x = x_{al.}|_0$, coincident locations. It is the familiar singularity associated with the Rayleigh problem, for example.

If equation (19) is integrated over the burn time, the final location of the outer oxide boundary is easily calculated

$$x_{oxd.}|_{burn} = \frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}L \tag{21}$$

This simply states that the final mass of oxidizer $\rho_{oxd.}x_{oxd.}|_{burn}$ is equal to $\frac{\gamma}{\alpha}$ times the initial mass of aluminum $\rho_{al.}L$, as required by the stoichiometry of (1). If the convection term in the equation for c, (7), is neglected, such global conditions, at different times, can bypass any discussion of v. Global mass considerations can also lead to the prediction of the final drop/particle radius for the spherical problem, but there the role of v is more profound because the generation of a radial oxide speed at the aluminum/alumina interface can not generate a mere solid body displacement, but must lead to a significant stress field. This is the subject of a later section.

Consider now the importance of the convection term in (7). Since $x \sim L$, $c \sim c_o$, and $v \sim \sqrt{\mathsf{D}/t}$ we have

$$v\frac{\partial c}{\partial x} \sim \frac{c_o}{t} \quad \text{and} \quad \mathsf{D}\frac{\partial^2 c}{\partial x^2} \sim \frac{c_o}{t} \tag{22}$$

and convection may not be neglected. But the time derivative has the same estimate, and so should be retained also; done properly, this is a 2-boundary Stefan problem with convection. Fortunately dynamics is not central to the problem, and this would not be the first time that a quasi-steady model has been adopted in circumstances for which it is but an extra-rational approximation. We can be reasonably sure that the qualitative picture that we have painted here is essentially sound, and the omitted time derivatives provide but quantitative corrections. Some measure of the magnitude of these corrections will be provided by numerical calculations described in the next section.

We finish this section by identifying the burn time when v is neglected, and $x_{oxd.}$ remains fixed at the initial value L. Then the solution for c is linear in x, vanishing at x_{al} and having the value c_o at L. Thus the diffusive flux to the reacting front is a simple function of $x_{al.}$, proportional to v_{rf}. In this way we find that the burn time is

$$t_{\text{burn}} = \frac{L^2}{2}\frac{\beta}{\alpha}\frac{\rho_{al.}}{\mathsf{D}c_o} \quad \text{(fast chemistry, quasi-steady, } v = 0) \tag{23}$$

which differs from (18) by the factor $(1 + \Gamma)$. In section 4 we compare this burn time and the burn time defined by (18) with numerical results obtained with v and $\partial c/\partial t$ retained.

3 Finite Chemistry Effects

In this section we start with the model of section 2 but modify it to account for finite-rate chemistry at the reaction front, so that c does not vanish there. The aluminum is liquid but how one should characterize the ensemble of O atoms is not clear. The constraints of the alumima molecules rob

it of the essential characteristics of a gas; nor is it a liquid. And so the reaction should probably be thought of as of the heterogeneous kind.

Global modeling of homogeneous gas-phase reactions has proven to be most valuable. If there are two reactants concentrations A, B, which, in a global sense react according to

$$\alpha A + \beta B \rightarrow \text{Products} \tag{24}$$

(i.e. this is not an elementary reaction) then, with a nod to the law of mass action and to the Maxwellian distribution of molecular speed (related to collision energy) we can model the reaction rate by

$$K = kA^{\mu}B^{\nu} \exp\left[-\frac{E}{RT}\right] \tag{25}$$

with suitably chosen values of k, μ, ν and E.

This can also work well for certain heterogeneous reactions; for example, experimental data for the chemical erosion of carbon by hot gases (relevant in nozzle erosion) has been fitted with similar formulas: a discussion with several references may be found in [13]. This is not too surprising. In one case gas molecules are colliding with gas molecules with a collision frequency that depends on the two concentrations; in the other, gas molecules are colliding with the surface of the carbon with a collision frequency that depends on the single concentration. In both cases the energy of the collisions is related to the high temperature tail of the Maxwellian.

We know of no authoritative discussion of a global kinetics model for our problem. However, it is not implausible to speculate that the rate at which aluminum atoms encounter O atoms depends on the concentration of the latter and, since we do not account for thermal effects so that the temperature dependence of the efficacy of such encounters is immaterial, we can take

$$K = kc^{\eta} \quad \text{at} \quad x = x_{al.} \tag{26}$$

to be the reaction rate. That is, with the choice $\eta = 1$, equation (6) is rewritten

$$\dot{M}_o = \frac{b}{a}\rho_{al.}v_{rf} = -(v + v_{rf})c_{rf} + \mathsf{D}\frac{\partial c}{\partial x}|_{rf} = kc_{rf} \tag{27}$$

With this modification, the analysis proceeds as in Section 2, so that we do not need to burden the reader with the details. The results are:

$$\begin{aligned}\left[\frac{\beta}{\alpha}\frac{\rho_{al.}}{k}v_{rf} - c_o\right]\left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}\exp\left(\frac{v}{\mathsf{D}}x_{oxd.}\right) - \exp\left(\frac{v}{\mathsf{D}}x_{al.}\right)\right] = \\ \left[\frac{\beta}{\alpha}\rho_{al.} + \frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}c_o\right]\left[\exp\left(\frac{v}{\mathsf{D}}x_{al.}\right) - \exp\left(\frac{v}{\mathsf{D}}x_{oxd.}\right)\right]\end{aligned} \tag{28}$$

where, as before,

$$\begin{aligned}v = v_{rf}\left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}} - 1\right] &= \frac{dx_{oxd.}}{dt} \\ v_{rf} &= -\frac{dx_{al.}}{dt}\end{aligned} \tag{29}$$

To examine equation (28) it is useful to introduce some scalings. To this end we write

$$x_{oxd.} = Ls_{oxd.}, \quad x_{al.} = Ls_{al.}, \quad v = \frac{\mathsf{D}}{L}u, \quad v_{rf} = \frac{\mathsf{D}}{L}u_{rf} \tag{30}$$

so that (28) becomes

$$\begin{aligned} c_o \left[\frac{\beta}{\alpha}\frac{\rho_{al.}}{c_o}\frac{\mathrm{D}}{kL} - 1\right]\left[\frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}\exp(us_{oxd.}) - \exp(us_{al.})\right] = \\ \left[\frac{\beta}{\alpha}\rho_{al.} + \frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}c_o\right]\left[\exp(us_{al.}) - \exp(us_{oxd.})\right] \end{aligned} \tag{31}$$

In the fast chemistry limit we recover the results of section 2. In the slow chemistry limit ($k \to 0$) u vanishes so that the exponentials can be simplified, and (31) leads to

$$u_{rf}\left[\frac{\beta}{\alpha}\frac{\mathrm{D}}{kL} + (s_{oxd.} - s_{al.})\left[\frac{\beta}{\alpha} + \frac{\gamma}{\alpha}\frac{\rho_{al.}}{\rho_{oxd.}}\frac{c_o}{\rho_{al.}}\right]\right] \sim \frac{c_o}{\rho_{al.}} \tag{32}$$

which, when $\mathrm{D}/kL \gg 1$, leads to

$$u_{rf} \sim \frac{\alpha}{\beta}\frac{c_o}{\rho_{al.}}\frac{kL}{\mathrm{D}} \quad \text{i.e.} \quad v_{rf} \sim \frac{\alpha}{\beta}\frac{c_o}{\rho_{al.}}k \tag{33}$$

Then $c_{rf} = c_o$ (there is no gradient of oxygen in the oxide), and the burning law is a linear one; the only relevant speed is k:

$$t_{\mathrm{burn}} = \frac{L\beta\rho_{al.}}{\alpha c_o k} \quad \text{(slow chemistry)} \tag{34}$$

This familiar result mirrors Glassman's discussion for gas-phase burning, [14]. Note that quite independently of the simple limit solution for c, the scalings show that the ratio of the diffusion term to both the time derivative and the convection term is

$$O\left[\frac{\mathrm{D}}{kL}\frac{\rho_{al.}}{c_o}\right]$$

and so the neighborhood of this limit may be discussed within a purely diffusive framework.

4 Numerical Results

In section 2 we deduced that the quasi-steady burn time in the fast chemistry limit is $L^2/2\Lambda$ (equation (18)); in the same limit but with v neglected it is $L^2\beta\rho_{al.}/2\alpha\mathsf{D}c_o$ (23); and in section 3 we deduced that the burn time in the slow chemistry limit is $(\beta L\rho_{al.})/(\alpha k c_o)$ (34). Consider the parameter choices

$$\begin{aligned} c_o = 6.4\mathrm{kg/m}^3 \quad k = 18.75\mathrm{m/s} \quad \mathrm{D} = 10^{-5}\mathrm{m}^2/\mathrm{s} \quad \rho_{al.} = 2400\mathrm{kg/m}^3 \quad \rho_{oxd.} = 3950\mathrm{kg/m}^3 \\ \alpha = 54 \quad \beta = 48 \quad \gamma = 102 \end{aligned} \tag{35}$$

Then the limit burn times are

$$1.91 \times 10^7 L^2 \text{ s} \quad \text{eq(18)} \qquad 1.67 \times 10^7 L^2 \text{ s} \quad \text{eq(23)} \qquad 17.78L \text{ s} \quad \text{eq(34)} \tag{36}$$

In the log-log plane the first and third of these define two straight lines which intersect at $L = .931 \times 10^{-6}$, with $kL/\mathrm{D} = 1.75$; order 1 values of kL/D characterize the transition from the linear burn law to the quadratic law. This transition is more accurately described using numerical simulations in which the time derivatives are retained.

In doing this we note that the system is stiff, because of the small value of $c_o/\rho_{al.}$, so that an explicit solver, such as Runge-Kutta, is inadequate. We used a Crank-Nicholson scheme, and the results are shown in Figure 4. The straight lines cross at $L = 10^{-6}$, $kL/\mathrm{D} = 1.9$, slightly different from the conclusions using the analytical results. At $L = 10^{-9}$ the analytically derived burn time is 1.78×10^{-8} in close agreement with the numerical result. At a burn time of 1 the analytically derived value of L from eq(18) is 2.29×10^{-4}; from eq(23) it is 2.45×10^{-4}. In both cases the errors are quite small.

5 Summary

In the past sections we have examined the familiar shrinking-core model in the planar context in order to highlight several features that do not appear to have been adequately discussed in the past. One is the speed v acquired by the alumina because of the addition of mass (aluminum and O) at the reaction front. It should be noted that if Rai et al, [4], are correct in arguing that the reacting front or domain lies within the alumina, then there will be convective fluxes of alumina away from the domain on both sides as alumina is added by reaction, necessarily tearing apart existing alumina molecules, and there would be substantial material stresses associated with this. But, as we shall see in the next section, there are substantial stresses associated with the creation of alumina in the context of the model that we adopt when the geometry is spherical so that simple solid-body displacement of the alumina, as in the planar problem, is not possible.

A second point that we have discussed is the role of the convection term and the time derivative in defining the distribution of c, the O concentration. Technically, both should be retained in the fast-chemistry limit, as both terms are comparable to the diffusion term. However, the time scale is defined by v_{rf}, not v, and for aluminum burning v is roughly 1/7 of $v_r f$. Then an error of 15% caused by omitting the convection term may not be of much significance if D is not well known. There is no good *a priori* reason for omitting $\partial c/\partial t$, but there also the error is small, at least for the values used in aluminum combustion.

6 The Spherical Problem

In this section we turn from the planar geometry to the spherical one. Here equations (1)-(6) are still applicable, as is (7) when the diffusion term is written in spherical form, but the oxide speed v presents difficulties, since it no longer corresponds to a solid-body displacement unless we suppose that the alumina is rigid. To calculate v we have to consider the displacement and stress fields in the oxide, and that is our focus.

Consider a sphere of liquid aluminum surrounded by a shell of alumina. As before we assume that the reaction surface is at the boundary between the two materials without assumption as

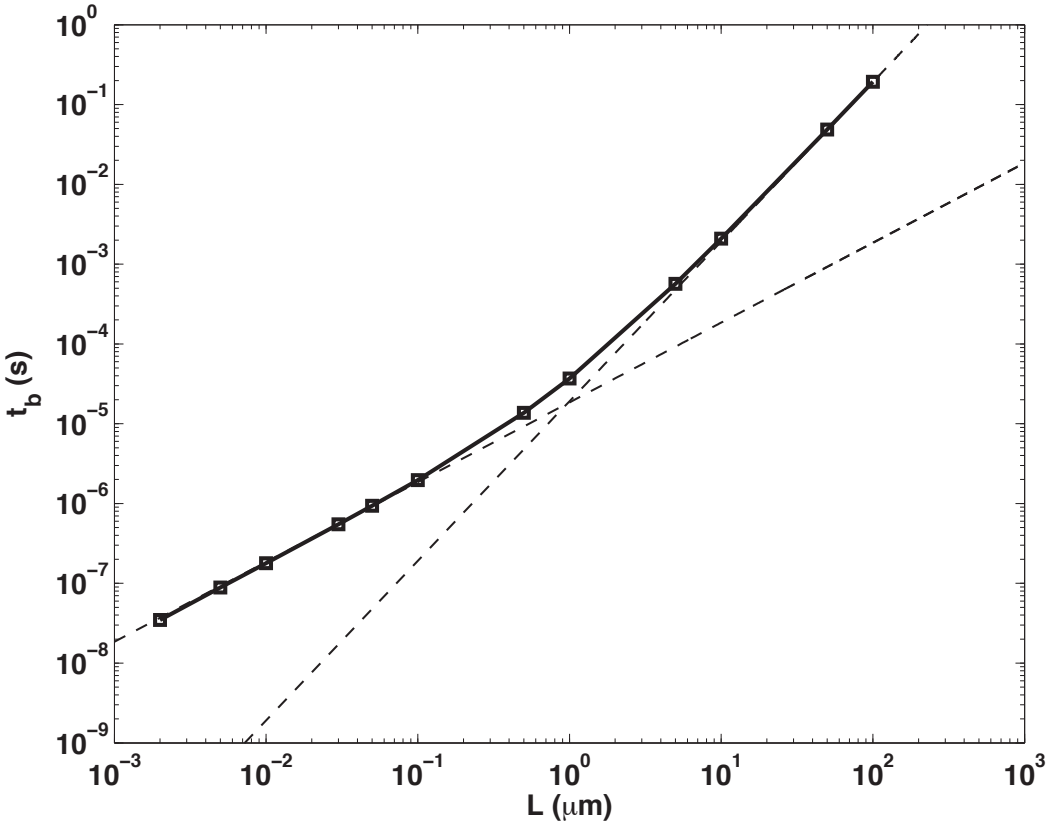

Figure 2: Burn Times

to what controls the reaction, whether it be diffusion of O through the oxide, or reaction at the aluminum surface. We assume that the reacting surface moves inwards with speed v_{rf}, and that the creation of alumina at the surface leads to an outward flux of alumina from the surface with local speed v. We calculate the stress consequences of this by considering an elastic shell of outer radius b and inner radius a. a decreases with time because of the aluminum consumption, and we shall assign this function. b changes for two reasons: the volume of oxide generated is greater than the volume of aluminum consumed; elastic displacement.

Considering just the first, if the initial radii are b_0 and a_0, and the final value of b is b_f ($a_f = 0$) then

$$b_f^3 = b_0^3 + \left(\frac{102}{54}\frac{\rho_{al.}}{\rho_{oxd.}}\right) a_0^3. \tag{37}$$

b_0 is greater than a_0 by an amount s, the thickness (small) of the genesis oxide layer. Then it is trivially shown that

$$\frac{b_f}{b_0} < 1.047 \tag{38}$$

and we shall neglect this change.

As for the elastic displacement, our calculations are within the framework of linear elasticity, and so that is also neglected.

The pressure in the external environment is taken to be P_b and that in the core region P_a. The presence of aluminum in the core plays no role except that its contribution to the reaction provides a relation between v_{rf} and v, as before. In what follows r is the radius, σ is Poisson's Ratio, E is Young's Modulus, τ_r is the radial stress, τ_1 and τ_2 are hoop stresses, δ is the radial displacement, ϵ_1 and ϵ_2 are the hoop strains, and ϵ_r is the radial strain.

The solutions of the linear equations of elasticity for this configuration are

$$\begin{aligned}
\tau_r &= \frac{1}{(b^3 - a^3)}\left[P_a a^3 - P_b b^3 + \frac{a^3 b^3 (P_b - P_a)}{r^3}\right] \\
\tau_1 = \tau_2 &= \frac{1}{(b^3 - a^3)}\left[P_a a^3 - P_b b^3 - \frac{a^3 b^3 (P_b - P_a)}{2r^3}\right] \\
\delta &= \frac{r}{E(b^3 - a^3)}\left[(1-2\sigma)(P_a a^3 - P_b b^3) - \frac{1+\sigma}{2r^3} a^3 b^3 (P_b - P_a)\right] \\
\epsilon_1 = \epsilon_2 &= \frac{\delta}{r}, \qquad \epsilon_r = \frac{\partial \delta}{\partial r}
\end{aligned} \tag{39}$$

These formulas can be derived in a straightforward fashion from the equations of linear elasticity, but may be found in [15]. They were used by Rosenband, [16], to examine the stresses on the genesis layer of amorphous alumina created when the aluminum particle is ignited and the aluminum expands.

The radial velocity associated with the displacement δ is

$$\frac{\partial \delta}{\partial t}|_r \quad \text{which is equal to} \quad v \quad \text{when evaluated at} \quad r = a \tag{40}$$

These solutions would normally be used to calculate the displacement and stress fields when P_a and P_b are assigned. But in our problem we are interested in the assignment of the radial velocity

at the inner radius a and the assignment of P_b, with P_a to be determined as the driver for v. P_a, like a, will be a function of time.

Rather than differentiate the formula for δ with respect to t we shall use a as a surrogate for time, with

$$a = b - v_{rf}t \quad \text{since} \quad a(0) = b \tag{41}$$

where we shall take v_{rf} (and therefore v, see (12)) to be constant.

So we differentiate δ with respect to a holding r constant, and then set $r = a$. Thus

$$A\frac{d\phi}{d\alpha} + B\phi + C = \frac{E(1-\alpha)}{P_b}\frac{\partial\delta}{\partial a}|_{r=a} = \frac{E(1-\alpha)}{P_b}\left(-\frac{v}{v_{rf}}\right) \tag{42}$$

where

$$\phi = \frac{P_a}{P_b}, \qquad \alpha = \frac{a^3}{b^3} \tag{43}$$

and the coefficients are given by the formulas

$$\begin{aligned} A &= 3\alpha\left[\alpha(1-2\sigma) + \frac{1}{2}(1+\sigma)\right] \\ B &= \frac{3\alpha}{(1-\alpha)}\left[\alpha(1-2\sigma) + \frac{1}{2}(1+\sigma)\right] + 3\alpha(1-2\sigma) + \frac{3}{2}(1+\sigma) \\ C &= -\frac{\alpha}{(1-\alpha)}\frac{9}{2}(1-\sigma) - \frac{3}{2}(1+\sigma) \end{aligned} \tag{44}$$

Before we can solve equation (42) we need to identify the initial value of P_a. For this purpose we shall suppose that there is a genesis layer of amorphous oxide of thickness 5nm and that the particle, of temperature 300K, is placed in an atmosphere of temperature greater than or equal to the aluminum melting temperature. Because the particle is small and its thermal conductivity high, it is assumed that its temperature is raised instantly to the atmospheric value, and so experiences a significant increase in volume which imposes stresses on the alumina. This is a problem that has been examined before, [9].

For this problem the thin-shell approximations to equations (39) are valid. Thus, writing

$$(b-a) = s, \quad r = a + \gamma s \tag{45}$$

we have, for s small

$$\begin{aligned} \tau_r &\sim -P_a + \gamma(P_a - P_b) \\ \tau_1 = \tau_2 &\sim \frac{1}{6}\frac{a}{t}(P_b - P_a) \\ (P_a - P_b) &\sim \frac{2Et}{a(1-\sigma)}\frac{\delta}{a} \end{aligned} \tag{46}$$

Then with $E = 300$GPa, σ=0.25, δ/a=.04 (corresponding to a liquid aluminum density of 2400kg/m^3, a solid aluminum density of 2700kg/^{3}), and $s/a = 1/16$ we have

$$(P_a - P_b) \sim 2\text{GPa}, \quad \tau_1 = \tau_2 \sim -5.3\text{GPa} \tag{47}$$

Then, to solve (42) we take

$$\frac{v}{v_{rf}} = 0.148 \qquad E = 300 \text{ GPa} \qquad \sigma = 0.25 \qquad P_b = 2 \times 10^6 \text{ Pa} \qquad P_a = 2\text{GPa} \tag{48}$$

where the last two are initial conditions applied at $\alpha = 0.834$.

Figure 6 shows the variations of ϕ with a/b. From this we see that the internal pressure rises significantly as the ball of aluminum shrinks. In this connection we note that Campbell *et.al.*[3] conducted a molecular dynamics study of the early stages of the oxidation of solid aluminum and found that significant internal pressures were generated. And Rai *et.al.* [4] were motivated by this work to impose pressure gradients in their study of combustion with both O diffusion and Al diffusion.

Once ϕ is known we can calculate the stresses and the strains. Figure 6 shows the strains (vs a/b) at $r = a$ and $r = b$

$$\begin{aligned} \frac{\delta}{a}|_a &= \frac{1}{(1-\alpha)} \frac{P_b}{E} \left[(1-2\sigma)(\phi\alpha - 1) - \frac{1+\sigma}{2}(1-\phi) \right] \\ \frac{\delta}{b}|_b &= \frac{1}{(1-\alpha)} \frac{P_b}{E} \left[(1-2\sigma)(\phi\alpha - 1) - \frac{1+\sigma}{2}\alpha(1-\phi) \right] \end{aligned} \tag{49}$$

And figure 6 shows the hoop stresses at $r = a$ and $r = b$.

$$\begin{aligned} \tau_{1,2}|_{r=a} &= \frac{P_b}{(1-\alpha)} \left[\phi\alpha - 1 - \frac{1}{2}(1-\phi) \right] \\ \tau_{1,2}|_{r=b} &= \frac{P_b}{(1-\alpha)} \left[\phi\alpha - 1 - \frac{1}{2}\alpha(1-\phi) \right] \end{aligned} \tag{50}$$

Clearly, when a becomes sufficiently small the strains and stresses can not be sustained by the alumina, and fracture must occur, albeit not in the neighborhood of the outer surface. The breaking of spherical symmetry in this way must have a significant impact on the burning rate.

6.1 A Fractal Hypothesis

In our earlier discussion of the planar model we identified the well-known results that the fast-chemistry limit gives rise to a $d^2 - t$ law, whereas the slow-chemistry limit gives rise to a $d - t$ law. Experiments on sub-micron burning, however, give laws that differ subtantially from these. Thus Parr et al, [17] report a $d^{0.3} - t$ law for combustion in steam; and Allen et al, [18] report a $d^{0.35} - t$ law for air, a $d^{0.24} - t$ law for a $CO_2/H_2O/N_2$ mixture.

Parr et al, [17], discuss agglomeration problems for their burner experiments, and we understand from anonymous sources that some believe that agglomeraton could be responsible for these small-n laws. But one would think that the agglomerations would need to be fractal in nature to generate

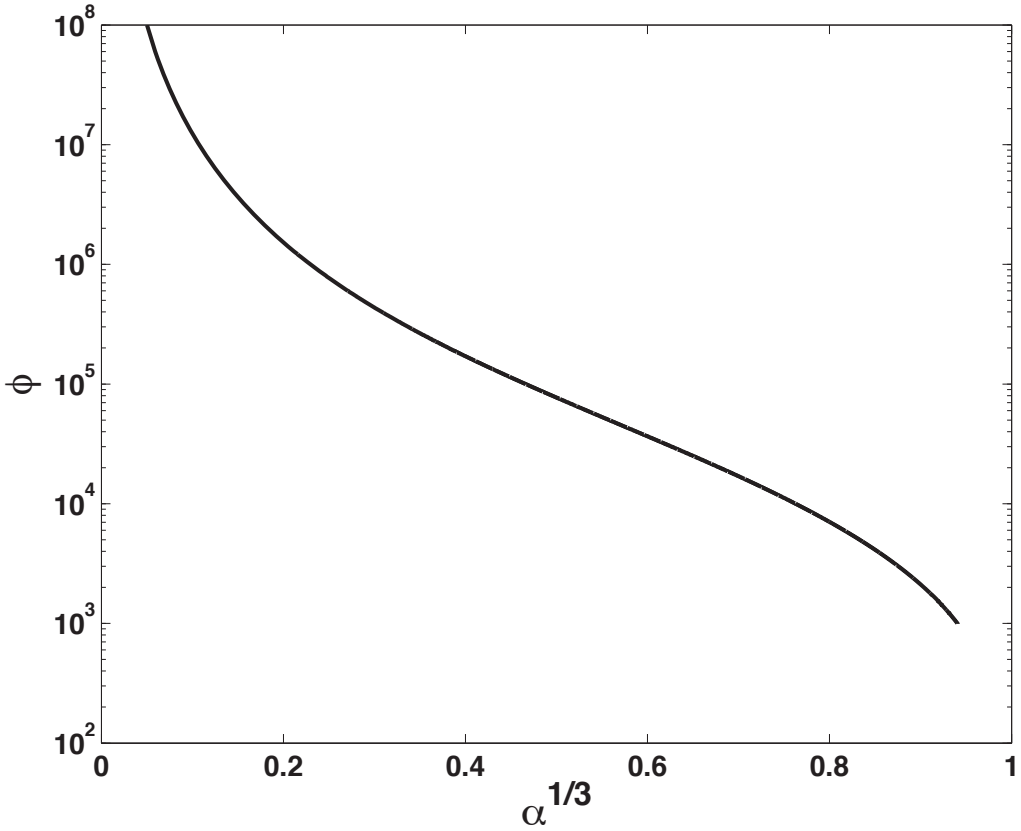

Figure 3: ϕ vs a/b

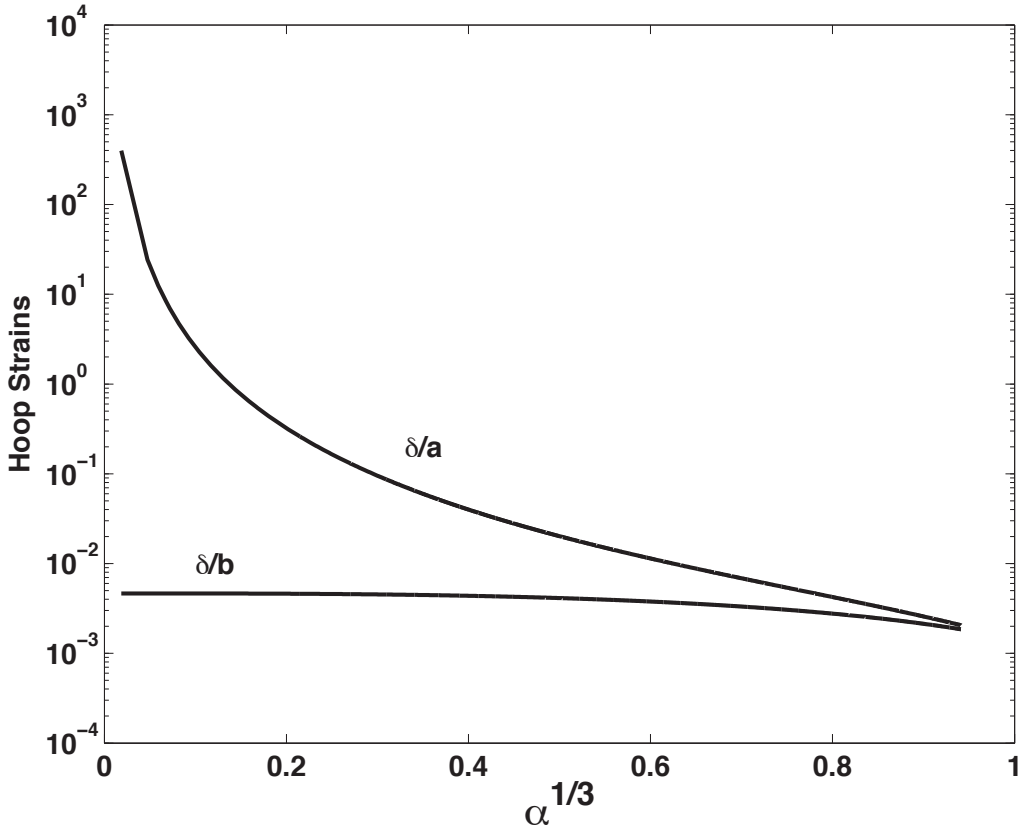

Figure 4: Strains vs. a/b

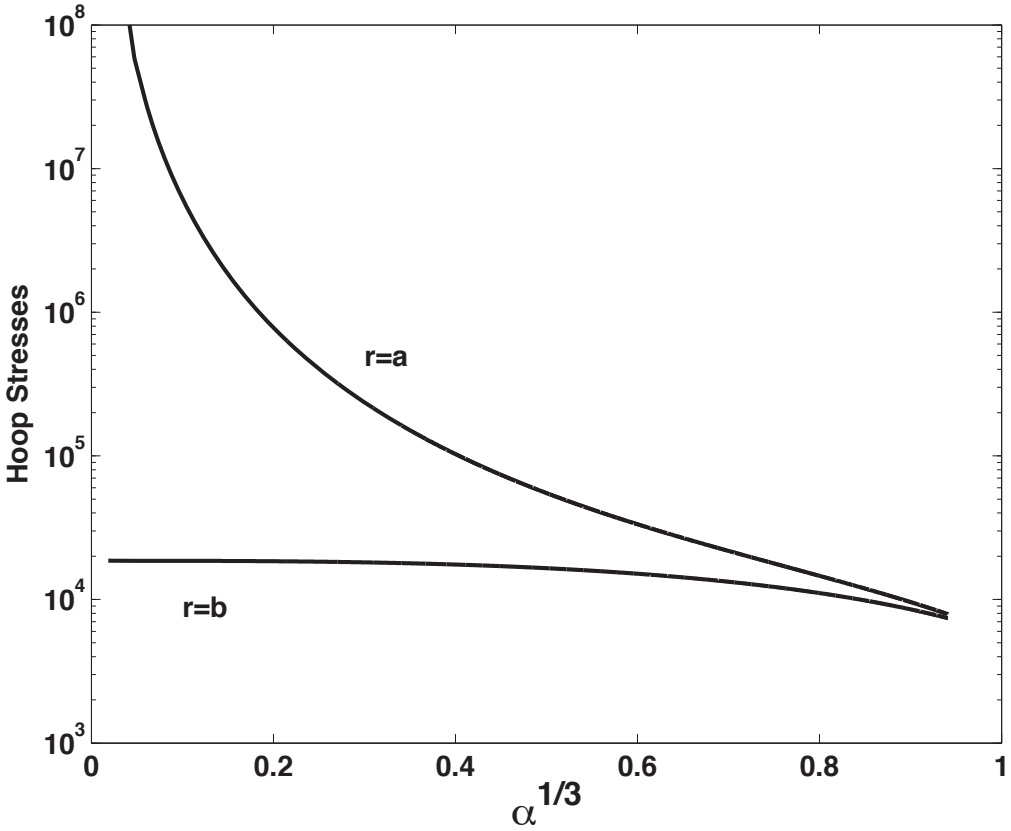

Figure 5: Hoop stresses vs. a/b

such an effect. Allen et al, [18], examine drop burning behind a reflected shock wave, and Allen (private communication) concludes, using conservative collision estimates, that agglomeration is negligible in that context. And so here we propose a different mechanism.

It is reasonable to suppose that the large hoop stresses generated as the aluminum/alumina front moves inwards will lead to extensive cracking. It is well known that large cracks in metals can be fractal in nature, and one might speculate that this is also true for the cracks in the small particles of interest to us. Should that be the case, the front will be fractal in nature.

Suppose we are in the slow chemistry regime and the radius of the aluminum core is s which changes with time according to

$$\frac{ds}{dt} = -K(\{\Xi\}, \mathsf{D}, T_{rf}) \tag{51}$$

where $\{\Xi\}$ is the complete set of parameters that characterize the ambient conditions and the properties of the aluminum and the alumina, and T_{rf} is the temperature at the reaction front. (We used a special case for K in section 3 in which the ambient state controls c_o, which in turn controls c_{rf}). We assume that, overall, the dependence of K on s (via T_{rf} for example) is small.

Equation (51) can be written as

$$\frac{d}{dt}\left[\frac{4}{3}\pi s^3\right] = -4\pi s^2 K \tag{52}$$

which expresses the obvious fact that the rate of change of the aluminum volume is proportional to the aluminum surface area. This is valid for a sphere with a smooth surface area. But if the alumina is cracked, aluminum will be forced into the cracks by pressure gradients and, perhaps, surface tension effects and, since the cracks would be thin, this would substantially increase the aluminum/alumina contact area. If s is now redefined to be the mean volume radius

$$\left(\frac{3}{4\pi}V\right)^{\frac{1}{3}}$$

where V is the total aluminum volume, equation (45) can be rewritten as

$$\frac{d}{dt}\left[\frac{4}{3}\pi s^3\right] = -4\pi s^{2+\nu} K \tag{53}$$

for some parameter ν which accounts for the enhanced area. This choice is motivated by the concept of a fractal area (in 3D space) of dimension $2+\nu, 0 < \nu < 1$ in which as ν goes to zero the area dimension approaches that of a smooth surface, and as ν goes to 1 the area is so rough, on a wide range of scales, that its dimension approaches that of a volume.

Equation (53) implies a $d^{1-\nu} - t$ law so that, for example, $\nu = 0.65$ leads to a $d^{0.35} - t$ law.

7 Conclusions

In this paper we have examined a simple one-dimensional model problem of aluminum combustion within the framework of the shrinking core model; and the spherical problem. The conclusions of the first problem are summarized in Section 5, and we note here that the one-dimensional framework permits a full discussion of the role of v, the speed generated within the oxide by the

O and Al reaction, together with unsteady effects. Such matters can not be considered for the spherical problem, because v can not be discussed without accounting for the large strain fields that it generates. However, using the linear equations of elasticity we can estimate these strains if we assign a speed to the reacting front. We conclude that internal strains generated thereby are sufficient to crack the oxide interior. If we then assume that the crack surfaces are fractal in nature, we are led to burn laws $d^n - t$ for which n can be significantly smaller than 1.

References

[1] S. Yagi, D.Kunii. 5th Symposium (International) on Combustion,Reinhold, NY, 1955, 231-244.

[2] Levenspiel, O. Chemical Reaction Engineering, 3rd edition, chapter 25 John Wiley and Sons.

[3] T.Campbell, R.Kalia, A.Nakano, P.Vashishta. Physical Review Letters, *Dynamics of Oxidation of Aluminum Nanoclusters using Variable Charge Molecular-Dynamics Simulations on Parallel Computers* 82(24) 1999 4866-4869.

[4] A.Rai, K.Park, L.Zhou, M.R.Zachariah Combustion Theory and Modelling *Understanding the mechanism of aluminum nanoparticle oxidation* 10(5) 2006 843-859.

[5] M.A.Trunov, M.Schoenitz, E.L.Dreizin. Combustion Theory and Modelling *Effect of polymorphic phase transformations in alumina layer on ignition of aluminum particles* 10(4) 2006 603-623.

[6] P. Hancock, R.C. Hurst, in: Advances in Corrosion Science and Technology, vol. 4, Plenum Press, New York, 1974, 184.

[7] J. Stringer, Corros. Sci. 10 (1970) 513.

[8] M.S. Hunter, P.J. Fowle, J. Electrochem. Soc. 103 1956 482.

[9] V. I. Levitasa, B.W. Asay, S.F. Son, M.Pantoya. Journal of Applied Phyics *Mechanochemical mechanism for fast reaction of metastable intermolecular composites based on dispersion of liquid metal* 101, 2007.

[10] P. Lynch, G. Fiore, H. Krier, and N. Glumac. Combust. Sci. and Tech. *Gas Phase Reaction in Nanoaluminum Combustion* 182 2010 842857.

[11] M.W.Beckstead *A Summary of Aluminum Combustion* paper presented at the RTO/VKI Special Course on "Internal Aerodynamics in Solid Rocket Propulsion", held in Rhode-Saint-Genese, Belgium, 27-31 May 2002, and published in RTO-EN-023.

[12] P. Lynch, H. Krier, N. Glumac. Proceedings of the Combustion Institute *A correlation for burn time of aluminum particles in the transition regime* 32 2009 18871893.

[13] P.Thakre, V.Yang. J. of Propulsion and Power *Chemical Erosion of Carbon-Carbon/Graphite Nozzles in Solid-Propellant Rocket Motors* 24(4) 2008 822-833.

[14] I.Glassman. Combustion, 3rd ed. AcademicPress, SanDiego, CA.(1996) Chapter6.

[15] Allan F. Bowes, 'Applied Mechanics of Solids' a free web book with URL solidmechanics.org. A modified version is published by Taylor and Francis, 2010.

[16] V.I.Rozenband, N.I. Vaganova. Combustion and Flame *A Strength Model of Heterogeneous Ignition of Metal Particles* 88 1992 113-118.

[17] T. Parr, C. Johnson, D. Hanson-Parr, K. Higa, K. Wilson. Thirty-Ninth JANNAF Combustion Subcommittee Meeting (2003)

[18] D. Allen, J. Kalman, H. Krier, and N. Glumac. *Nano-aluminum combustion temperature and burning time dependence on particle size at elevated pressures* Spring Technical Meeting of the Central States Section of the Combustion Institute April 2224, 2012

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